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(71) Applicants
Mitsubishi Monsanto Chemical Co. Ltd.
(Incorporated in Japan)
5-2 Marunouchi 2-chome, Chiyoda-ku, Tokyo, Japan.
Mitsubishi Chemical Industries Ltd.
(Incorporated in Japan)
5-2 Marunouchi 2-chome, Chiyoda-ku, Tokyo, Japan

(72) Inventors
Kouji Sumino
Fumikazu Yajima
Toshihiko Ibuka
Fumio Orito

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(74) Agent and/or Address for Service
Mewburn Ellis & Co.,
2/3 Cursitor Street, London EC4A 1BQ

(54) A single crystal of IIIb–Vb compound, particularly GaAs, and method for producing the same

(57) A single crystal of IIIb–Vb group compound contains $1 \times 10^{17} \sim 8 \times 10^{19}$ cm^{-3} of oxygen and has a dislocation density which is low and uniform in a direction perpendicular to the growth direction.

An LEC method for crystal growth of a single crystal of GaAs comprises an addition of oxide at an oxygen concentration of $1 \times 10^{17} \sim 2 \times 10^{21}$ cm^{-3}.

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SPECIFICATION

A single crystal of IIIb-Vb compound, particularly GaAs, and method for producing the same

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a IIIb-Vb group compound single crystal (hereinafter referred to as "IIIb-Vb single crystal"), particularly to a gallium arsenide (GaAs) single crystal having a low dislocation density, and a production method thereof, in particular, to a liquid encapsulated Czochralski method (hereinafter referred to as the "LEC method"). The single crystal GaAs has a high electron mobility and hence is widely used for an UHF or SHF element, a high-speed switching element, and a substrate of integrated circuit (IC) ("Information Processing" *25* (1) pp 37–46 (1984) by Hideki Hasegawa).

2. Description of the Related Arts

The properties required of a IIIb-Vb single crystal, such as GaAs, when used as the above electronic elements and IC substrate, are a high level of purity, a high degree of crystalline perfection, and uniform electrical properties. A semi-insulative property is necessary for the IC substrate.

Dislocation, which degrades the crystalline perfection, causes malfunctions in ICs. Thus, in order to use the IIIb-Vb single crystal for a substrate of highly integrated ICs and high output FETs having a large chip area, a IIIb-Vb single crystal having a low dislocation density is first produced and then cut into wafers. The LEC method is used for producing a GaAs single crystal for use as the substrate of an IC or the like, since the thus-produced GaAs has a large diameter and a high level of purity needed to enhance the activation rate of ions implanted in a GaAs substrate (BULLETIN OF THE JAPAN INSTITUTE OF METALS. Vol 23 (1984), No. 7, pp 586~592).

In the LEC method, the B_2O_3 melt, which is an encapsulant, covers the surface of the melt of IIIb-Vb group command. The temperature gradient across the layer of the B_2O_3 melt can amount to 100°C/cm, and hence is considered high as compared with the horizontal boat growth method. The GaAs single crystal pulled from the GaAs melt undergoes great thermal stress during passage through the layer of the B_2O_3 melt. This thermal stress is one cause of the generation of a number of dislocations in the IIIb-Vb single crystal. The disclocation density, in terms of etch pit density (EPD) of the GaAs single crystals produced by the LEC method, generally ranges from approximately 10^4 to 10^5 cm^{-2}. The dislocation distribution of GaAs single crystals produced by the LEC method, in a plane perpendicular to the pulling-up direction, is such that it is highest around the periphery, and is at its next highest level in the center of the IIIb-Vb single crystals. The disclocation density, therefore, may be seen as a W shape, in which a low dislocation-density region is formed around the center and is encompassed by the outer, highest dislocation-density regions.

B. Jacob describes in "Semi-Insulating III-V Materials" S. Makram-Ebid et al. Ed. p. 2~18 (1984) Shiva Publishing Ltd., a method for decreasing the dislocation by adding indium, which is an electrically neutral impurity, to the GaAs. According to this method, a GaAs single crystal is pulled up from the melt, to which metallic indium has been added in an amount of from 10^{18} to 10^{20} cm^{-3}, and the dislocation density is drastically decreased by this In addition.

The present inventors investigated the dislocation density of IIIb-Vb single crystals produced by the LEC method, and found a drastic reduction occurred in EPD of (100). Nevertheless, in several GaAs single crystals, etch pits arranged linearly in the <110> direction around the periphery were discovered, and EPD occasionally exceeded 1×10^4 cm^{-2} in the region containing the etch pits.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a IIIb-Vb single crystal which is free of locally high EPD and thus has a low EPD through the crystal.

It is another object of the present invention to improve an LEC method for the growth of a IIIb-Vb group compound, thereby preventing locally high EPD in a plane perpendicular to the pulling direction.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

IIIb-Vb Single Crystal

The IIIb-Vb single crystal according to the present invention is characterized by containing from 1×10^{17} to 8×10^{19} cm^{-3} of oxygen.

When the oxygen concentration of the IIIb-Vb single crystal is less than 1×10^{17} cm^{-3}, the amount of linear etch pits becomes appreciable, and thus the phenomenon of locally high EPD

cannot be prevented. On the other hand, when the oxygen concentration exceeds 8×10^{19} cm^{-3}, the crystalline properties are degraded. The compounds of IIIb-Vb group are GaAs, InAs and InP.

The In concentration of the IIIb-Vb single crystal is preferably from 1×10^{18} to 1×10^{20} cm^{-3}. At the In concentration less than 1×10^{18} cm^{-3}, the EPD tends to increase. On the other hand, when the In concentration of the GaAs single crystal exceeds 1×10^{20} cm^{-3}, the IIIb-Vb single crystal tends to embrittle and disadvantageous precipitation and the like of In tends to occur. A more preferred In concentration is from 2×10^{19} to 5×10^{19} cm^{-3}.

GaAs Single Crystal Containing Oxygen and Indium

This GaAs single crystal can be produced by growing GaAs from a GaAs melt, to which from 1×10^{19} to 1×10^{21} cm^{-3} of In and from 1×10^{18} to 2×10^{21} cm^{-3} of oxygen are added. The preferred added concentrations of In and oxygen are from 2×10^{20} to 5×10^{21} cm^{-3}, and from 1×10^{18} to 3×10^{19} cm^{-3}, respectively. The addition concentration herein indicates the number of atoms of In or oxygen added to 1 cm^3 of the melt. When the addition concentrations lie outside the ranges mentioned above, the preferred In concentration and requisite oxygen concentration cannot be ensured in the GaAs single crystal.

The addition of In and oxygen to the GaAs melt is preferably carried out by using indium oxide (In_2O_3). In this case, the indium oxide is added to obtain an In concentration of from 1×10^{19} to 1×10^{21} cm^{-3} in the GaAs melt. Alternatively, In and oxygen may be separately added. In this case, In in the metallic form, and oxygen in the from of As (III) oxide (As_2O_3) and gallium oxide (Ga_2O_3) are added to the melt to obtain the requisite concentrations in the melt.

The crystal growth method used for growing the GaAs single crystal from the melt, to which In and oxygen are added, is preferably the LEC method using an encapsulant, such as B_2O_3 or the like, since a high oxygen concentration in the melt can be thus attained, contamination of the melt by a crucible and an encapsulant is slight, and productivity is high. This crystal growth method could be used in a boat growth method, such as a gradient freeze method or horizontal Bridgeman method.

During the crystal growth, impurities, such as Si, S, Cr, and the like, which determine the electrical properties, may or may not be added to the melt. The undoped, semi-insulative GaAs single crystal which does not contain the impurities at all, is appropriate as a substrate for UHF or SHF elements and ICs.

The crystal growth direction is preferably in the <100> direction, since a round substrate is thus obtained. The crystal growth direction, however, may be <111>.

LEC Method for Growing Single Crystal of IIIb-Vb Compound

The LEC method for growing a IIIb-Vb single crystal using an encapsulant, according to the present invention, is characterized by adding at least one oxide selected form the group consisting of oxide of the IIIb-group element and oxide of the Vb group element to the melt of the IIIb-Vb group compound at an oxygen concentration of at least one oxide of from 1×10^{18} to 2×10^{21}, preferably from 1×10^{19} to 1×10^{21} per cm^3 of the melt of the IIIb-Vb group compound.

When the IIIb-Vb group compound is GaAs, the oxide of the IIIb element is preferably gallium oxide (Ga_2O_3) and the oxide of the Vb element is preferably diarsenic trioxide.

When the IIIb-Vb group compound is GaP, the oxide is preferably Ga_2O_3.

When the IIIb-Vb group compound is InP, the oxide is preferably In_2O_3.

When the IIIb-Vb group compound is InAs, the oxide of the IIIb element is preferably In_2O_3 and the oxide of the Vb element is preferably As_2O_3.

A special LEC growth device is not required for carrying out the method according to the present invention, and a usual such device may be used. A preferable crucible is made of PBN (pyrolitic boron nitride) or is coated with PBN, since the contamination of the melt by the crucible is slight. Graphite is less preferable but may be used as the material of a crucible or vessel.

The heating is usually carried out by means of a graphite resistance-heater having a cylindrical or wine-glass shape. The temperature gradient in the LEC growth device may be adjusted, if necessary, by disposing a heat-shield made of graphite or a cylindrical heater above the crucible or vessel. The interior of LEC growth apparatus is pressurized, during the crystal growth, to a pressure of usually from 10 to 60 kg/cm^2 (gauge pressure) by using an inert gas, such as argon or nitrogen. As the liquid sealant, high purity boron oxide (B_2O_3) thoroughly desiccated is ordinarily used.

When commencing the growth of a IIIb-Vb single crystal, a predetermined amount of B_2O_3 and polycrystalline IIIb-Vb compound are loaded in a crucible or the like. How ver, instead of loading the IIIb-Vb compound, a m tallic IIIb element and elem ntary Vb in an amount slightly greater than the stoichiometric amount may be loaded. In this case, the IIIb-V melt is formed during heating and temperature-elevating the crucible or the like.

Subsequently, at least one of the oxid of the IIIb group element, e.g., gallium oxide (Ga_2O_3), and the oxide of the Vb group el m nt, e.g., diarsenic trioxide (As_2O_3), is loaded into the

crucible or the like. The addition amount of Ga_2O_3 and/or As_2O_3 is not the analysis value but the calculation value, namely such that the number of oxygen atoms of Ga_2O_3 and/or As_2O_3 added amounts to a concentration of from 1×10^{18} to 2×10^{21}, preferably 3×10^{19} to 3.5×10^{20}, per cm^3 of the melt. When the oxygen concentration is less than 1×10^{18} cm^{-3}, it is difficult to decrease the dislocation density of the obtained IIIb-Vb single crystal. On the other hand, when the oxygen concentration exceeds 2×10^{21} cm^{-3}, a IIIb-Vb single crystal is difficult to obtain, and even if a IIIb-Vb single crystal is obtained, crystal defects, such as dislocations, are disadvantageously increased.

Ga_2O_3 and As_2O_3 may be added alone or together at an optional proportion to one another. An equal molar ratio of Ga_2O_3 and As_2O_3 is preferred, because this suppresses the generation of vacancies.

The conditions for LEC growth other than those described above are the same as usual.

The IIIb-Vb single crystal produced by the method according to the present invention has a dislocation density, in terms of EPD, lower than that obtained by conventional methods, and attains an EPD of 5000 cm^{-2} or less. In the IIIb-Vb single crystal produced by the method according to the present invention, the distribution of dislocations in a plane perpendicular to the pulling direction is uniform.

The present invention is further explained with reference to the examples and comparative examples.

In the examples and comparative examples, the LEC crystal puller used was an "MSR-6" type manufactured by the Cambridge Instruments Co., Ltd. of Britain.

EPD was measured by dipping test samples in fused potassium hydroxide at 350°C for 20 minutes and then counting the amount of etch pits, under a microscope.

The oxygen concentration of wafers was measured by using a secondary-ion mass analysis device "CAMECA 3F" type manufactured by the Thomson CFS Co., Ltd. of France.

The In concentration of the wafers was measured by using an atomic absorption analyzer "AAS-4000" type produced by the "Perkinson-Elmer" Co., Ltd. of the U.S.A.

Example 1

500 g of Ga, 550 g of As, 4.5 g of In_2O_3 (corresponding to the In addition concentration of 1×10^{20} cm^{-3} and the oxygen addition concentration of 1.5×10^{20} cm^{-3}) and 150 g of B_2O_3 were contained in a crucible made of PBN (pyrolitic boron nitride) and having an inner diameter of 100 mm. The interior of the LEC crystal puller was pressurized to 65 kg/cm^2 (gauge pressure) and the crucible was heated to 1400°C to form the GaAs melt. The crucible temperature was then lowered to 1350°C. While the crucible and a seed crystal were rotated, the seed crystal was brought into contact with the GaAs melt and then pulled upwards to attain a growth of a GaAs single crystal in the <100> direction. The obtained GaAs single crystal has a weight of 650 g and diameter of 50 mm. A (100) wafer was cut from the top end of a straight body portion of the single crystal and subjected to the EPD measurement. The EPD of the wafer, except for a 6 mm wide outer peripheral part, was 900 cm^{-2} in average and 1100 cm^{-2} at greatest. No linearly arranged etch pits were detected.

The In concentration of the wafer was 9.5×10^{18} cm^{-3} and the oxygen concentration of the wafer was 8×10^{17} cm^{-3}.

Example 2

The procedure of Example 1 was repeated to produce the GaAs single crystal, except that instead of In_2O_3 added in the case of Example 1, 1.89 g of metallic In and 3.2 g of As_2O_3 (the In addition concentration was 5×10^{19} and the oxygen addition concentration was 1.5×10^{20} relative to cm^3 of the GaAs melt) were added.

A (100) wafer was cut from the top end of a straight body portion of the single crystal and subjected to the EPD measurement. The EPD of the wafer, except for a 6 mm wide outer peripheral part, was 1200 cm^{-2} in average and 1500 cm^{-2} at greatest. No linearly arranged etch pits were detected.

The In concentration of the wafer was 5×10^{18} cm^{-3} and the oxygen concentration of the wafer was 6×10^{17} cm^{-3}.

Comparative Example 1

The procedure of Example 1 was repeated to produce the GaAs single crystal, xc pt that instead of the In_2O_3 added in the case of Example 1, 3.7 g of metallic In (the In addition concentration was 9.95×10^{19} relative to cm^3 of the GaAs melt) was added.

A (100) waf r was cut from the top end of a straight body portion of the single crystal and subjected to th EPD measurement. The EPD of the wafer, except for a 6 mm wide outer peripheral part, was 1000 cm^{-2} in average and 5000 cm^{-2} at greatest. Linearly arranged etch pits were detected at portions of the wafer wh re the EPD was greater than 1000 cm^{-2}.

The In concentration of the wafer was 1×10^{18} cm^{-3} and the oxygen concentration of the

wafer was 2×10^{16} cm^{-3}.

Example 3

1500 g of Ga, 1631.6 g of As, 1.5 g of Ga_2O_3, 1.58 g of As_2O_3, and 600 g of B_2O_3 were contained in a crucible made of PBN and having an inner diameter of 150 mm. The interior of the LEC growth device was pressurized to 65 kg/cm^2 (gauge pressure) and the crucible was heated to 1400°C to form the GaAs melt. The pressure was then reduced to 20 kg/cm^2. While the crucible and a seed crystal were rotated at 10 rpm in an anticlockwise direction and 8 rpm in a clockwise direction, respectively, the seed crystal was brought into contact with the GaAs melt and then pulled upwards at a speed of 7 mm/h to attain a growth of a GaAs single crystal in the <100> direction. The obtained GaAs single crystal had a weight of 2000 g and a diameter of 80 mm.

A {100} wafer was cut from the top end of a straight body portion of the single crystal where the fraction solidified was 0.10. The fraction solidified indicates a weight ratio of the ingot portion at a side adjacent to the seed crystal and above the wafer relative to the whole ingot. The wafer was subjected to measurement of the EPD and resistivity. Epd was uniform throughout the wafer, including its peripheral portion, and was 1500 cm^{-2} Neither linage (linear defects) nor defects by precipitates were detected throughout the wafer. The resistivity exhibited a tendency to decrease at an outer peripheral portion of the wafer, but was 1×10^{7} Ω·cm or higher throughout the major portion of the wafer.

Another {100} wafer was cut from a straight body portion of the single crystal where the fraction solidifed was 0.61 and subjected to the EPD measurement. The EPD was slightly high, but the average EPD taken from eight points across the diameter of the wafer was 2400 cm^{-2}, and the highest EPD was 2850 cm^{-2}.

Comparative Example 2

The same crystal growth procedure of Example 3 was repeated except that Ga_2O_3 and As_2O_3 was not added.

A wafer was cut from an upper straight body portion of the ingot where the fraction solidified was 0.12 and subjected to the EPD measurement. The average EPD taken from nine points across the diameter of the wafer was 10500 cm^{-2}, and the minimum and highest EPDs were 6000 cm^{-2} and 25000 cm^{-2}, respectively.

CLAIMS

1. A single crystal of IIIb-Vb group compound having a low dislocation density, characterized by containing from 1×10^{17} to 8×10^{19} cm^{-3} of oxygen.

2. A single crystal of IIIb-Vb group compound according to claim 1, which consists of gallium arsenide.

3. A single crystal of gallium arsenide according to claim 2, which contains from 1×10^{18} to 1×10^{20} cm^{-3} of indium.

4. A single crystal of IIIb-Vb group compound according to claim 1, 2, or 3, wherein said single crystal is produced by single crystal growth from a melt of said IIIb-Vb group compound, which contains from 1×10^{18} to 2×10^{21} cm^{-3} of oxygen atom.

5. A single crystal of IIIb-Vb group compound according to claim 4, wherein said single crystal is grown by liquid encapsulated Czochralsky method.

6. A method for producing a single crystal of a IIIb-Vb group compound from a melt of the IIIb-Vb group compound by a liquid encapsulated Czochralsky method, characterized in that at least one oxide selected from the group consisting of an oxide of said IIIb group-element and an oxide of said Vb group-element is added to said melt at an amount of from 1×10^{17} to 2×10^{21} of oxygen atoms of said oxide(s) per cm^3 of said melt.

7. A method according to claim 6, wherein said IIIb-Vb group element GaAs and said group consists of gallium oxide and diarsenic trioxide.

8. A method according to claim 7, wherein gallium oxide and diarsenic trioxide are added at equal molar amounts.

9. A method according to claim 6, 7, or 8, wherein indium oxide is added to said melt.

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